

Synthesis of TBP-coated magnetic Pst-DVB particles for uranium separation*

WANG Huan (王欢),¹ SHAO Xian-Zhang (邵宪章),¹ TIAN Qing (田青),¹ and JI Yan-Qin (吉艳琴)^{1,†}

¹China CDC Key Laboratory of Radiological Protection and Nuclear Emergency,

National Institute for Radiological Protection, Chinese Center for Disease Control and Prevention, Beijing 100088, China

(Received February 14, 2014; accepted in revised form March 25, 2014; published online June 20, 2014)

Magnetically assisted chemical separation process is an efficient method used widely in separating radionuclides and heavy metals in environmental samples. It is simple, compact and cost-effective, with less secondary waste streams. Tributyl phosphate (TBP)-coated magnetic poly (styrene-divinylbenzene) (Pst-DVB) nano-particles were synthesized and characterized by transmission electron microscopy, scanning electron microscopy, vibrating sample magnetometer, thermogravimetry and Fourier transform infrared spectrometry. The application of TBP-coated magnetic Pst-DVB particles in separating low concentration of uranium from aqueous media was evaluated, and the equilibrium adsorption isotherm was investigated. Our results indicate that the TBP-coated magnetic Pst-DVB particles may be of potential application for uranium separation.

Keywords: Magnetic particles, Synthesis, Uranium, Adsorption isotherm

DOI: [10.13538/j.1001-8042/nst.25.030301](https://doi.org/10.13538/j.1001-8042/nst.25.030301)

I. INTRODUCTION

The rapid development of nuclear industry in China in recent years arises increased concerns on management of radioactive wastes, which contain uranium isotopes in various concentrations and oxidation states [1]. Uranium is of high toxicity [2, 3] and has long half-life isotopes, and its separation from radioactive waste is of importance in reducing potential harm to human health and environment.

While solvent extraction, ion exchange and extraction chromatography are mainly used to separate uranium from different samples, magnetically assisted chemical separation (MACS) process, which combines magnetic separation with the high selectivity afforded by solvent extractants, was developed for separating heavy metals elements [4, 5]. The advantages of MACS include its high separation efficiency, cost-effectiveness and reduced secondary waste streams [6]. The MACS method has been in rapid development. In Argonne Laboratory, for example, researchers used polymeric magnetic particles coated with organic extractants (CMPO, TBP, TOPO, Cyanex 272, or Cyanex 301) to separate actinides [7], uranium [8], transuranic element [5, 9] and the harmful metallic elements [10] in certain conditions. Also, magnetic particles containing crystalline silicotitanates (CST) were used to separate cesium from milk [11]; HEDPA solution [12] and polymer magnetic particles coated with Cyanex 923, DMDTDMA, and TODGA were used to separate lanthanide and actinide elements [13–15]; and silanized magnetic particles with CMPO/TBP coating were for europium separation [16].

In this work, preparation of polymer-magnetic particles coated with poly (styrene-divinylbenzene) (Pst-DVB) and an adsorbed layer of TBP (tributyl phosphate) were prepared and

characterized. Their capability of removing uranium from aqueous solutions was evaluated.

II. EXPERIMENTAL

A. Materials

Uranium standard (GBW(E) 070173) solution was obtained from National Research Center for Certified Reference Materials, Beijing, China. TBP in purity of >99.0% was produced by Fluka. All chemicals, including styrene (Tianjin Fuchen Chemical Reagents Factory, China), divinyl benzene (J&K Chemica, China), ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$) (Tianjin Shuangchuan Chemicals, China), ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4 \text{H}_2\text{O}$), ammonia water (25%), benzoyl peroxide(BPO) (Shantou Xilong Chemical Factory, China), ethanol, oleic acid, lauryl sodium sulfate (Beijing Chemical Works, China), were of analytical grade and used without any further purification.

B. Preparation of magnetic fluid

Magnetic fluid was prepared by conventional co-precipitation method with some modifications [17]. $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ (23.6 g) and $\text{FeCl}_2 \cdot 4 \text{H}_2\text{O}$ (8.6 g) were dissolved in 500 mL deionized water under nitrogen gas and vigorous stirring at 80 °C. $\text{NH}_3 \cdot \text{H}_2\text{O}$ (25 mL, 25 wt.%) was added to the solution. Then, oleic acid (10 mL) was added drop wise into the suspension within 20 min. After several minutes, the magnetic precipitates (Fe_3O_4 magnetic nanoparticles) were isolated from the solvent by magnetic decantation. The precipitates were washed with deionized water for several times to remove the excess oleic acid. The magnetic precipitate can be re-dispersed in water to form a water liquid based magnetic fluid.

* Supported by the National Natural Science Foundation of China (No. 20477058), Chinese Ministry of Health (No. 201002009), and the Chinese Ministry of Science and Technology (No. 2013BAK03B00)

† Corresponding author, jiyanqin@nirp.cn

C. Preparation of magnetic Pst-DVB particles

Styrene (150 mL) was mixed with 10 mL DVB, 20 g magnetic fluid and 1 g BPO to form an organic phase. SDS (0.2 g) was dissolved in 500 mL deionized water. The two mixtures were mixed together to form a suspension, which was transferred to a 500 mL beaker equipped with four vertical stainless steel paddles, a condenser, a nitrogen inlet, and a stirrer. The mixture was heated to 60 °C in 1 hour and maintained for 2 hours. The reaction continued for 2 hours at 70 °C, stirring at 400 rpm. The magnetic microspheres were separated by magnetic decantation and washed with deionized water and acetone several times.

D. TBP coating

The magnetic particles were washed repeatedly with deionized water and 0.1 M NaOH solution, and dried overnight in a fume hood prior to use. TBP (0.25 mL) was diluted in 2 mL ethanol, and mixed with 0.1 g magnetic particles. The mixture was placed in a sonicating bath for 10 min, and heated in a water bath at 100 °C, stirred constantly, until the ethanol was evaporated. The particles were baked in an oven at 120 °C for 17 hours to obtain the TBP-coated magnetic Pst-DVB particles [18].

E. Characterization

Size and morphology of the uncoated Fe_3O_4 particles and the magnetic Pst-DVB particles were examined by transmission electron microscopy (TEM, JEM 2100). The magnetic Pst-DVB particles before and after TBP coating were examined by scanning electronic microscopy (SEM, JSM-6700F). The magnetization curves of the samples were measured with a vibrating sample magnetometer (VSM, PPMS-9). The magnetite content of the magnetic polymer microspheres was determined by thermogravimetry (Netzsch, STA449). FTIR spectra were taken using a Fourier transform infrared spectrometer (Jasco FT/IR-660 plus).

F. Extraction process

The extraction efficiency was evaluated using the distribution coefficient, K_d . Portions of uranium standard solution (100 mg/L) and appropriate volumes of ultrapure water were mixed in 5 mL test tubes. Then, 30 mg of TBP-coated magnetic Pst-DVB particles were added under mixing and the total volume of suspension was made up to 3.0 mL. The suspensions were mixed at room temperature. Subsequently, TBP-coated magnetic Pst-DVB particles were separated from the suspension using a permanent NdFeB magnet and uranium concentration in the clear supernatant was measured using inductively coupled plasma mass spectrometry (ICP-MS, Element2). The uranium concentration was determined from the calibration curve, which was prepared by determining a series

of diluted uranium standard solution with 2% (v/v) HNO_3 . The K_d was calculated by

$$k_d = \frac{(C_i - C_e)V}{C_e m} \quad (\text{mL/g}), \quad (1)$$

where C_i and C_e are respectively the initial and equilibrium uranium concentrations in the aqueous phase, V is the total volume of the suspension (3 mL), and m is the weight (30 mg) of the added TBP-coated magnetic Pst-DVB particles.

All the experiments were performed twice and mean values were used in data analysis. Control experiments without the TBP-coated magnetic Pst-DVB particles were carried out to determine the degree of uranium removal.

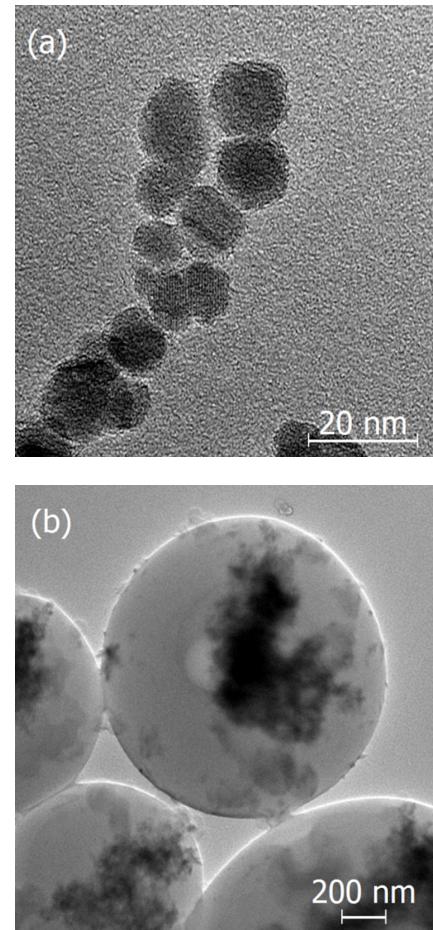


Fig. 1. TEM images of the Fe_3O_4 magnetic nanoparticles (a) and magnetic Pst-DVB particles (b).

III. RESULTS AND DISCUSSION

A. Characterization

Structure of the synthesized Fe_3O_4 and Pst-DVB magnetic particles were examined using the transmission electron microscope (TEM). The Fe_3O_4 nanoparticles were of spherical structure, in relatively uniform size (Fig. 1(a)) of around

10 nm, while the Pst-DVB particles, containing the Fe_3O_4 nanoparticles (Fig. 1(b)), were sized at about 1 μm .

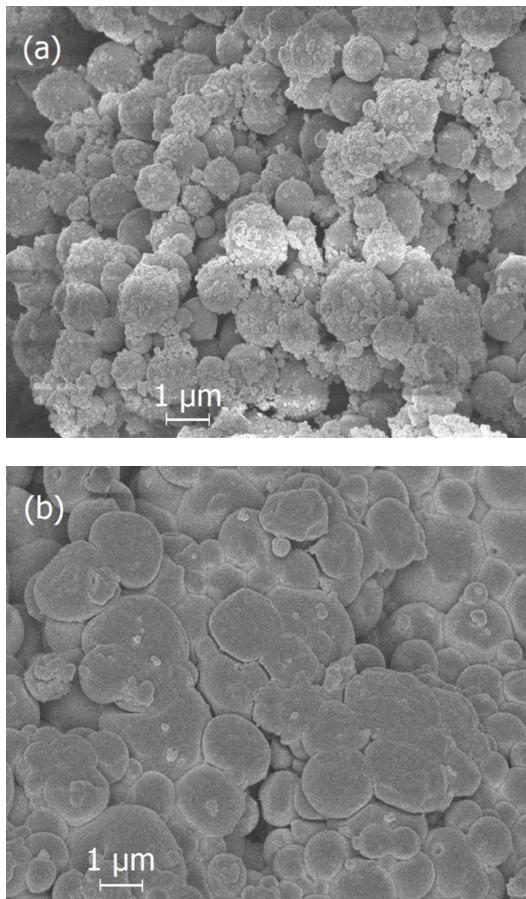


Fig. 2. SEM images of magnetic Pst-DVB particles before (a) and after (b) TBP-coating.

Morphologies of Pst-DVB particles before and after the TBP-coating were examined by scanning electron microscope (SEM) (Fig. 2). The SEM images indicated that the TBP-coating changed the surface morphology of Pst-DVB particles.

There was no hysteresis in the magnetization with both remanence and coercivity being zero, showing that the Fe_3O_4 magnetic nanoparticles and TBP-coated magnetic Pst-DVB particles are superparamagnetic (Fig. 3). Magnetization of the Fe_3O_4 magnetic nanoparticles was saturated at 39.41 emu/g. After polymerization of the DVB and styrene, and the coating process of TBP, saturation magnetization of the TBP-coated magnetic Pst-DVB particles reduced to 4.32 emu/g. This is due to the embedment of Fe_3O_4 magnetic nanoparticles inside the magnetic polymer microspheres, the increased particle size, and the decreased unit mass content of magnetic particles.

Figure 4 shows TGA curve of the TBP-coated magnetic Pst-DVB particles. At 600 $^{\circ}\text{C}$, organic substances of the TBP-coated magnetic Pst-DVB particles decomposed, with just the magnetic Fe_3O_4 being left, the content of which was about 10% of the TBP-coated magnetic Pst-DVB particles.

From the FTIR spectra of the Pst-DVB particles before and after TBP-coating (Fig. 5), the characteristic peaks at 1600 cm^{-1} , 1449 cm^{-1} , 760 cm^{-1} and 700 cm^{-1} are of styrene. And a band at around 627 cm^{-1} and 585 cm^{-1} is assigned to Fe–O. In Spectrum (b), the band at 1028 cm^{-1} corresponding to P–O–C group indicates the presence of TBP. Also, the P=O group of TBP can be seen at 1264 cm^{-1} .

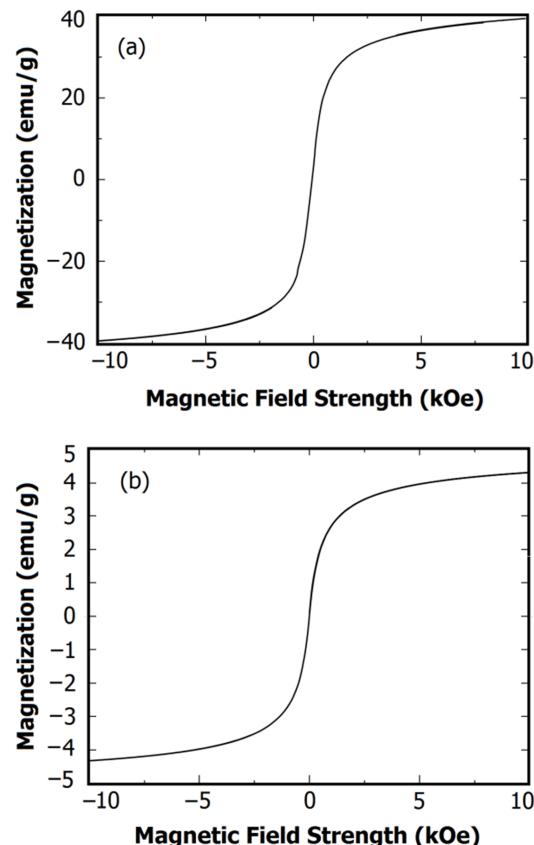


Fig. 3. VSM magnetization curves of (a) Fe_3O_4 magnetic nanoparticles and (b) TBP-coated magnetic Pst-DVB particles.

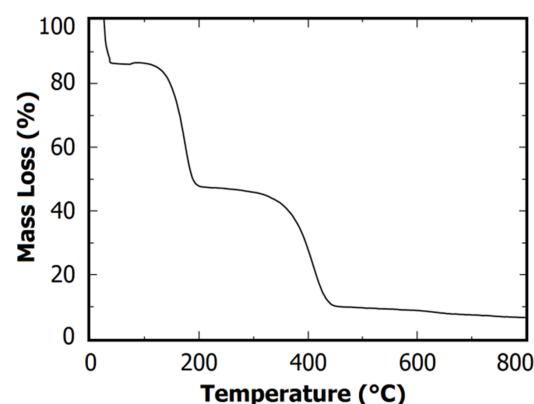


Fig. 4. TGA curve of the TBP-coated magnetic Pst-DVB particles.

B. Effect of HNO_3 concentrations on uranium uptake by TBP-coated magnetic Pst-DVB particles

Uptake of uranium in 0.05 mg/L concentration by the TBP-coated magnetic Pst-DVB particles was studied with nitric acid in concentrations of 0.1–0.7 mol/L. The distribution coefficient of uranium, K_d (mL/g), increased with the HNO_3 concentration (Fig. 6), reaching a peak value of 109 mL/g at 5 mol/L HNO_3 and decreasing at higher HNO_3 concentrations. Therefore, the optimal initial nitric acid concentration of 5 mol/L was used for the TBP-coated magnetic Pst-DVB particles to remove uranium from water solutions.

C. Adsorption isotherms

Adsorption isotherm describes how a solute interacts with the adsorbent under equilibrium conditions, providing important information for understanding mechanism of the adsorption systems. Linear isotherm can be expressed as

$$q_{\text{eq}} = K_d C_{\text{eq}}, \quad (2)$$

where q_{eq} is the amount of adsorbed solute per unit weight of adsorbent (mg/g), K_d is the distribution coefficient (mL/g)

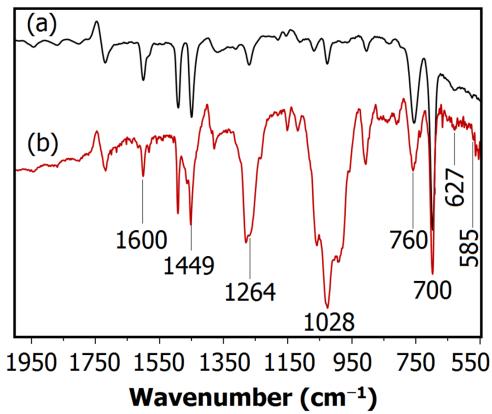


Fig. 5. (Color online) FT-IR spectra of the Pst-DVB particles before (a) and after (b) TBP-coating.

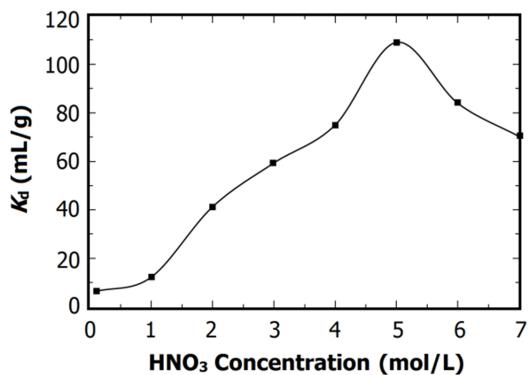


Fig. 6. K_d of uranium as function of aqueous HNO_3 concentration, using TBP-coated magnetic Pst-DVB.

and C_{eq} (mg/L) is the residual liquid phase concentration after equilibrium. If the number of adsorption sites is large relative to the number of solute molecules, it is possible to use the Freundlich isotherm. The model is based on the assumption that ions are accumulated infinitely on the sorbent as described by

$$q_{\text{eq}} = K_f (C_{\text{eq}})^{1/n}, \quad (3)$$

where K_f and n are the Freundlich constants and are indicators of adsorption capacity and intensity, respectively. If $n = 1$, the Freundlich isotherm is identical to the linear isotherm. By taking the log of the terms, a straight line develops making it easier to obtain the slope and intercept of the line

$$\log q_{\text{eq}} = \log K_f + (\log C_{\text{eq}})/n. \quad (4)$$

The linear and Freundlich isotherms were determined for uranium concentration of 0.2–1 mg/L and are given graphically in Fig. 7. The isotherm model parameters were obtained by non-linear least square fitting of the experimental data. We had $K_d = 0.0963$ ($R^2 = 0.9728$) by using the linear model to fit the data of uranium adsorption on the TBP-coated magnetic Pst-DVB particles, while $K_f = 0.1186$ and $1/n = 1.2391$ ($R^2 = 0.9975$) by using the Freundlich models. The Freundlich model fits the experimental data better, and the highest value of sorption capacity was 0.050 mg/g, but it was not possible to determine the maximum sorption capacity because the concentration range of uranium was below saturation.

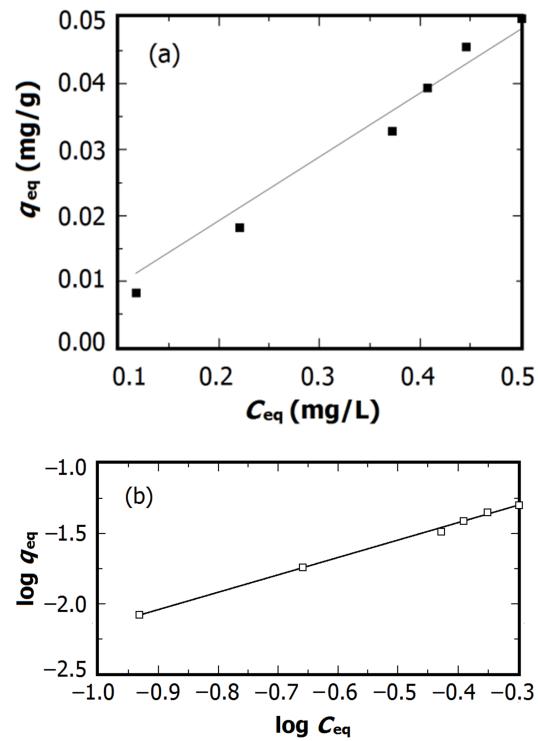


Fig. 7. Linear (a) and Freundlich (b) isotherms for uranium in 5 M HNO_3 absorbed by TBP-coated magnetic Pst-DVB particles.

IV. CONCLUSION

The synthesized TBP-coated magnetic Pst-DVB particles show characteristics of the P—O—C and P=O groups and the changes in surface morphology. The distribution coefficient of the TBP-coated magnetic Pst-DVB particles increases with HNO_3 concentration, reaching a peak value at 5 mol/L nitric

acid. The adsorption equilibrium data are fitted by the linear and Freundlich models, and the results show that the Freundlich model fits the data better. In addition, the TBP-coated magnetic Pst-DVB particles enable simple removal from the suspensions using a permanent magnet. These results indicate that the TBP-coated magnetic Pst-DVB particles can be used to separate uranium from aqueous media.

[1] Li Q, Cao X, Pang C, *et al.* *J Radioanal Nucl Ch*, 2012, **293**: 67–73.

[2] Anke M, Seeber O, Müller R. *Chem Erde-Geochem*, 2009, **69**: 75–90.

[3] Priest N D. *Lancet*, 2001, **357**: 244–246.

[4] International Atomic Energy Agency. Feasibility of Separation and Utilization of Caesium and Strontium from High Level Liquid Waste, Technical Reports Series No. 356, IAEA, Vienna, 1993, 30.

[5] Kaminski M D, Nunez L, Bradley C, *et al.* Argonne National Laboratory, ANL-95/1, 1995.

[6] Nuñez L, Vandegrift G F, Buchholz B A. *Separ Sci Technol*, 1995, **30**: 1455–1471.

[7] Nuñez L, Kaminski M, Aase S B, *et al.* *Separ Sci Technol*, 1996, **31**: 1393–1407.

[8] Kaminski M D and Nuñez L. *Separ Sci Technol*, 2000, **35**: 2003–2018.

[9] Kaminski M D, Landsberger S, Nuñez L, *et al.* *Separ Sci Technol*, 1997, **32**: 115–126.

[10] Kaminski M D, Nuñez L, Visser A E. *Separ Sci Technol*, 1999, **34**: 1103–1120.

[11] Kaminski M D, Nuñez L, Pourfarzaneh M, *et al.* *Sep Purif Technol*, 2000, **21**: 1–8.

[12] Kaminski M D and Nuñez L. *Sep Sci Technol*, 2002, **37**: 3703–3714.

[13] Shaibu B S, Reddy M L P, Bhattacharyya A. *J Magn Magn Mater*, 2006, **301**: 312–318.

[14] Shaibu B S, Reddy M L P, Prabhu D R, *et al.* *Radiochim Acta*, 2006, **94**: 267–273.

[15] Shaibu B S, Reddy M L P, Murali M S, *et al.* *Radiochim Acta*, 2007, **95**: 159–164.

[16] Yamaura M, Camilo R L, Felinto M C F C. *J Alloys Compd*, 2002, **344**: 152–156.

[17] Liu X Q, Liu H Z, Xing J M, *et al.* *China Part*, 2003, **1**: 76–79.

[18] Buchholz B A, Tuazon H E, Kaminski M D, *et al.* *Sep Purif Technol*, 1997, **11**: 211–219.